

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of: §  
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Michael D. Jensen § Examiner: Unassigned  
  
Serial No.: Unassigned § Atty. Docket No.: 33633US1  
  
Filed: July 19, 2001 §  
  
For: COMPOSITIONS THAT CAN §  
PRODUCE POLYMERS §  
§

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Please amend the application as follows:

**IN THE TITLE**

Please delete the title, and substitute "PROCESS FOR PRODUCING  
POLYMERS".

**IN THE SPECIFICATION**

On each page of the application, in the upper right hand corner of the page,  
please change the attorney docket number "33633US" and substitute "33633US1".

On page 1, line 1, please add "This application is a divisional of application Serial No. 09/080,619, now allowed".

On page 33, line 17, please delete "carton" and substitute therefor – carbon –.

Please delete the Abstract and substitute therefor:

—A process of using a catalyst composition to polymerize at least one monomer to produce a polymer. The process comprises contacting the catalyst composition and at least one monomer in a polymerization zone under polymerization conditions to produce the polymer. The catalyst composition is produced by a process comprising contacting at least one organometal compound, at least one treated solid oxide compound, and at least one organoaluminum compound. —

## **IN THE CLAIMS**

Please delete Claims 1-7, and 9-25.

Please amend Claim 8 as follows:

8. (amended) A process of using a catalyst composition to polymerize at least one monomer to produce a polymer, said process comprising contacting said catalyst composition and at least one monomer in a polymerization zone under polymerization conditions to produce said polymer;

wherein said catalyst composition is produced by a process comprising contacting at least one organometal compound, at least one treated solid oxide

compound, and at least one organoaluminum compound to produce said catalyst composition,

wherein said organometal compound has the following general formula



wherein  $M^1$  is selected from the group consisting of titanium, zirconium, and hafnium, and

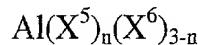
wherein  $(X^1)$  is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, and

wherein substituents on said substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and hydrogen; and

wherein  $(X^3)$  and  $(X^4)$  are independently selected from the group consisting of halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and

wherein  $(X^2)$  is selected from the group consisting of Group OMC-I or Group OMC-II, and

wherein said organoaluminum compound has the following general formula,



wherein  $(\text{X}^5)$  is a hydrocarbyl having from 1-20 carbon atoms, and

wherein  $(\text{X}^6)$  is a halide, hydride, or alkoxide, and

wherein "n" is a number from 1 to 3 inclusive;

wherein said treated solid oxide compound is produced by a process comprising contacting at least one solid oxide compound with at least one electron-withdrawing anion source compound; and

wherein said solid oxide compound is calcined before, during, or after contacting said electron-withdrawing anion source; and

wherein the activity of said catalyst composition is greater than 250 grams of polyethylene per gram of treated solid oxide compound per hour; and wherein there is a substantial absence of aluminoxanes and organoborates.

Please add the following claims:

26. A process according to Claim 8 wherein said polymerization conditions comprise slurry polymerization conditions.

27. A process according to Claim 26 wherein said contacting is conducted in a loop reactor zone.

28. A process according to Claim 27 wherein said contacting is conducted in the presence of a diluent that comprises, in major part, isobutane.

29. A process according to Claim 26 wherein said at least one monomer is ethylene.

30. A process according to Claim 26 wherein said at least one monomer comprises ethylene and an aliphatic 1-olefin having 3 to 20 carbon atoms per molecule.

31. A process according to Claim 8 wherein said treated solid oxide compound is produced by a process comprising:

- 1) contacting said solid oxide compound with said at least one electron-withdrawing anion source compound to form a first mixture; and
- 2) calcining said first mixture to form said treated solid oxide compound.

32. A process according to Claim 8 wherein said treated solid oxide compound is produced by a process comprising simultaneously calcining and contacting said solid oxide compound and said at least one electron-withdrawing anion source compound.

33. A process according to Claim 8 wherein said electron-withdrawing anion source compound is selected from the group consisting of sulfates, halides, and triflate.

34. A process according to Claim 8 wherein said calcining is conducted for about 1 hour to about 10 hours at a temperature in the range of about 400 to about 800° C.

35. A process according to Claim 8 wherein said treated solid oxide compound is produced by a process comprising increasing the acidity of said solid oxide compound by two, or more, electron-withdrawing anion source compounds in two, or more, separate steps.

36. A process according to Claim 35 wherein said treated solid oxide compound is produced by a process comprising:

- 1) contacting said at least one solid oxide compound with a first electron-withdrawing anion source compound to form a first mixture;
- 2) calcining said first mixture to produce a calcined first mixture;
- 3) contacting said calcined first mixture with a second electron-withdrawing anion source compound to form a second mixture; and
- 4) calcining said second mixture to form said treated solid oxide compound.

37. A process according to Claim 8 wherein said catalyst composition is produced by a process comprising:

- 1) contacting said organometal compound and said treated solid oxide compound together for about 1 minute to about 1 hour at a temperature of about 25 to about 100°C to form a first mixture; and
- 2) contacting said first mixture with an organoaluminum compound to form said catalyst composition.

38. A process according to Claim 8 wherein said catalyst composition

can polymerize ethylene into a polymer with an activity greater than 2000 (gP/(gS·hr)), and

wherein said organometal compound is selected from the group consisting of

bis(cyclopentadienyl) hafnium dichloride;  
bis(cyclopentadienyl) zirconium dichloride;  
[ethyl(indenyl)<sub>2</sub>] hafnium dichloride;  
[ethyl(indenyl)<sub>2</sub>] zirconium dichloride;  
[ethyl(tetrahydroindenyl)<sub>2</sub>] hafnium dichloride;  
[ethyl(tetrahydroindenyl)<sub>2</sub>] zirconium dichloride;  
bis(n-butylcyclopentadienyl) hafnium dichloride;  
bis(n-butylcyclopentadienyl) zirconium dichloride;  
((dimethyl)(diindenyl)silane) zirconium dichloride;  
((dimethyl)(diindenyl)silane) hafnium dichloride;

((dimethyl)(ditetrahydroindenyl)silane) zirconium dichloride;  
((dimethyl)(di(2-methyl indenyl)) silane) zirconium dichloride;  
bis(fluorenyl) zirconium dichloride, and  
wherein said organoaluminum compound is selected from the group  
consisting of

trimethylaluminum;  
triethylaluminum;  
tripropylaluminum;  
diethylaluminum ethoxide;  
tributylaluminum;  
triisobutylaluminum hydride;  
triisobutylaluminum;  
diethylaluminum chloride, and

wherein said solid oxide compound is selected from the group consisting of  
 $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CdO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  
 $\text{Mn}_2\text{O}_3$ ,  $\text{MoO}_3$ ,  $\text{NiO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{SnO}_2$ ,  $\text{SrO}$ ,  $\text{ThO}_2$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  
 $\text{WO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ; and mixtures thereof, and

wherein said treated solid oxide compound has been contacted with fluoride  
or chloride or both.

39. A process of using a catalyst composition to polymerize at least one  
monomer to produce a polymer, said process comprising contacting said catalyst

composition and said at least one monomer in a polymerization zone under polymerization conditions to produce said polymer;

wherein said catalyst composition is produced by a process comprising:

- 1) calcining alumina at 600°C for 3 hours and simultaneously contacting with carbon tetrachloride to produce a treated solid oxide compound;
- 2) combining said treated solid oxide compound with bis(n-butylcyclopentadienyl) zirconium chloride at a temperature in a range of about 25 to about 100°C to produce a mixture; and
- 3) about between 1 minute and 1 hour, combining said mixture and triethylaluminum to produce said catalyst composition.

40. A process of using a catalyst composition to polymerize at least one monomer to produce a polymer, said process comprising contacting said catalyst composition and said at least one monomer in a polymerization zone under polymerization conditions to produce said polymer;

wherein said catalyst composition is produced by a process comprising:

- 1) calcining an oxide selected from alumina, silica-alumina, aluminophosphate, and mixtures thereof to produce a calcined oxide;

- 2) contacting said calcined oxide with a treating agent selected from sulfating agents, fluoriding agents, and chloriding agents to produce a treated oxide;
- 3) combining (1) said treated oxide, (2) an organoaluminum compound selected from triethylaluminum, triisobutylaluminum, and mixtures thereof; and (3) an organometal compound.

41. A process according to Claim 40 wherein said organometal compound is bis(n-butylcyclopentadienyl) zirconium dichloride.

42. A process according to Claim 41 wherein said treating agent is a chloriding agent.

43. A process according to Claim 42 wherein said treating agent is carbon tetrachloride.

44. A process of using a catalyst composition to polymerize at least one monomer to produce a polymer, said process comprising contacting said catalyst composition and said at least one monomer in a polymerization zone under polymerization conditions to produce said polymer;

wherein said catalyst composition is produced by a process comprising:

- 1) calcining alumina to produce a calcined alumina;
- 2) treating said calcined alumina with carbon tetrachloride at an elevated temperature to give a treated alumina;

3) combining said treated alumina with triethylaluminum and bis(n-butylcyclopentadienyl) zirconium dichloride.

45. A process according to Claim 8 wherein said catalyst composition is produced by a process consisting essentially of contacting said organometal compound, said treated solid oxide compound, and said organoaluminum compound.

46. A polymer produced by the process of Claim 8.

47. A polymer produced by the process of Claim 39.

48. A polymer produced by the process of Claim 40.

49. A polymer produced by the process of Claim 44.

### **REMARKS**

For the convenience of the Examiner, Applicants provide the following information to show that each new claim is fully supported by the disclosure.

Claim 26: p.16, lines 8-10.

Claim 27: p.16, lines 10-11.

Claim 28: p.16, lines 11-12.

Claim 29: p.16, lines 4-5.

Claim 30: p.15, lines 19-20; p.16, lines 1-7.

Claim 31: p.10, lines 19-20; p.11, lines 1-4.

Claim 32: p.11, lines 4-6.

Claim 33: p.11, lines 8-12.

Claim 34: p.12, lines 9-14.

Claim 35: p.11, lines 13-15.

Claim 36: p.11, lines 15-20.

Claim 37: p.13, lines 8-13.

Claim 38: p.14, lines 17-20; p.15, line 1; p.8, lines 4-18; p.9, lines 11-19; p.12, lines 3-7; and p.11, lines 8-11.

Claim 39: p.13, lines 8-19; and Example 36.

Claim 40: p.12, lines 9-14, p.11, line 11; p.13, lines 1-3; p.9, line 13 and line 16.

Claim 41: p.8, line 12.

Claim 42: p.11, line 11.

Claim 43: Example 36.

Claim 44: Example 36.

Claim 45: p.3, line 16.

### CONCLUDING REMARKS

Applicants respectfully request that the Examiner enter this Preliminary Amendment into the record.

Respectfully submitted,

CHEVRON PHILLIPS CHEMICAL COMPANY LP

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### CERTIFICATE OF MAILING

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7/19/01

(Date)

Polly C. Owen  
Ginger K. Yount

**APPENDIX**

Please make the following changes:

**IN THE TITLE**

Please amend the title of the invention as follows:

[COMPOSITIONS THAT CAN PRODUCE] PROCESS FOR  
PRODUCING POLYMERS

**IN THE SPECIFICATION**

Please delete the Abstract and substitute the following therefor:

[This invention provides a compositions that are useful for  
polymerizing] A process of using a catalyst composition to polymerize at least one  
monomer [into at least one] to produce a polymer. The process comprises  
contacting the catalyst composition and at least one monomer in a polymerization  
zone under polymerization conditions to produce the polymer. The catalyst  
composition is produced by a process comprising contacting at least one  
organometal compound, at least one treated solid oxide compound, and at least  
one organoaluminum compound.

**IN THE CLAIMS**

Please delete Claims 1-7, and 9-25.

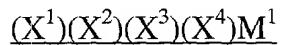
Please amend Claim 8 as follows:

8. (amended) A process of using [the] a catalyst composition [of claim 7] to  
polymerize at least one monomer[s] [into polymers] to produce a polymer, said

process comprising contacting said catalyst composition and at least one monomer in a polymerization zone under polymerization conditions to produce said polymer;[.]

wherein said catalyst composition is produced by a process comprising contacting at least one organometal compound, at least one treated solid oxide compound, and at least one organoaluminum compound to produce said catalyst composition,

wherein said organometal compound has the following general formula



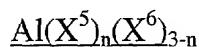
wherein  $M^1$  is selected from the group consisting of titanium, zirconium, and hafnium, and

wherein  $(X^1)$  is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, and

wherein substituents on said substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and hydrogen; and

wherein  $(X^3)$  and  $(X^4)$  are independently selected from the group consisting of halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and wherein  $(X^2)$  is selected from the group consisting of Group OMC-I or Group OMC-II, and

wherein said organoaluminum compound has the following general formula,



wherein  $(X^5)$  is a hydrocarbyl having from 1-20 carbon atoms, and wherein  $(X^6)$  is a halide, hydride, or alkoxide, and wherein "n" is a number from 1 to 3 inclusive;

wherein said treated solid oxide compound is produced by a process comprising contacting at least one solid oxide compound with at least one electron-withdrawing anion source compound; and

wherein said solid oxide compound is calcined before, during, or after contacting said electron-withdrawing anion source; and

wherein the activity of said catalyst composition is greater than 250 grams of polyethylene per gram of treated solid oxide compound per hour; and wherein there is a substantial absence of aluminoxanes and organoborates.